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Interplay of disorder and delocalization in photosynthetic light harvesting

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Photosystems, the machines of photosynthesis, are highly complex and energetically disordered pigment–protein structures. Yet, they perform their function, be it highly efficient energy transfer and charge separation or the ability to switch between light-harvesting and photoprotective states, extremely well. In this opinioned review we describe the interplay of disorder and exciton delocalization in photosynthetic light harvesting. By discussing recent research advances on grounds of well-established concepts, we demonstrate that not only is the excitation delocalization a robust phenomenon, but that it in fact enables the light-harvesting function in the disordered environment.

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Introduction

In photosynthetic light harvesting, sunlight is absorbed and the excitation energy is transferred through the photosynthetic apparatus to the reaction centre, where charge separation takes place. Interestingly, although occurring in a complex, fluctuating spatio-energetic landscape, these processes are very robust, with a quantum efficiency of transport plus charge separation approaching unity [1,2]. This remains something of a dream in artificial solar technology, where even in the crystalline semiconductors the energy/charge extraction remains to be an efficiency-limiting factor [3,4]. What is more, the light-harvesting complexes can have an extended built-in functionality, such as switching between light-harvesting and photoprotective states. It is worthwhile to confront the 'disordered' picture of 'biology' with the events that take place in highly ordered 'crystalline' structures that are often applied in solar materials. In this text we describe the fascinating interplay of excitation delocalization and energetic disorder, controlled by the protein environment, which determines the rate and efficiency of excitation transport.

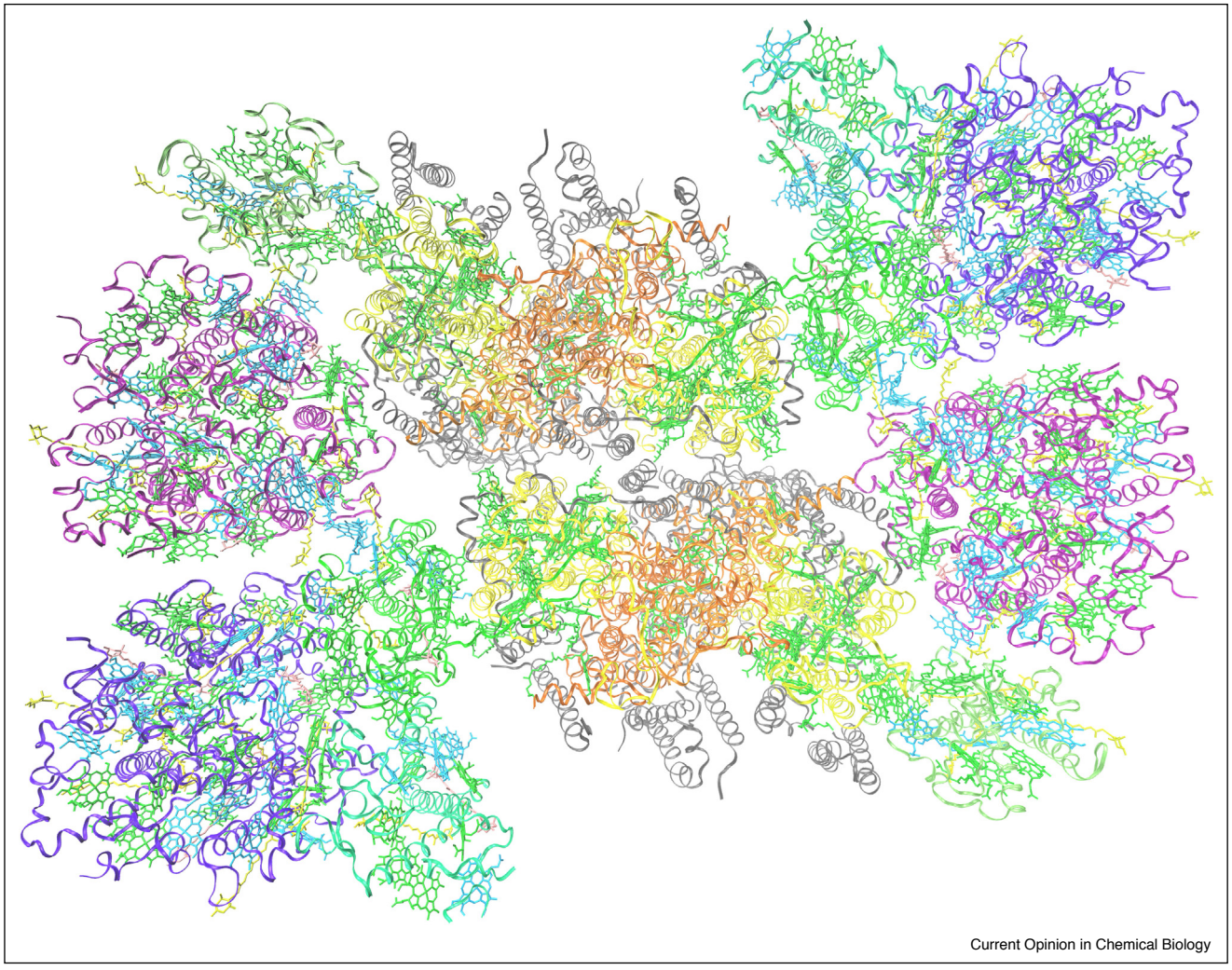
Photosynthetic light harvesting

Photosynthetic light harvesting is carried out by chlorophyll and carotenoid pigment molecules in specially synthesized pigment–protein complexes. The experiments by Emerson and Arnold in the thirties showed that there is way more chlorophyll pigments than reaction centers, introducing the concept of the photosynthetic unit [5]. This implies that almost all the absorbed light is captured outside of the reaction center. Furthermore, because no large number of chemical intermediates was found in the photosynthetic membrane, the excitation energy has to be transferred through the photosystem to the reaction center. This transport was discovered and first described by Duysens in the fifties, who considered the excitation hopping between individual pigments [6,7]. Using Förster theory [8] for concentrated randomly oriented homogeneous chlorophylls, he was able to estimate the time needed for a single jump and calculated that the excitation can make hundreds of jumps. Today, owing to X-ray crystallography and cryo-electron microscopy, the structure of most light harvesting systems is known [9–11]. The pigment organization is not random and the pigments have fixed positions and orientations to enable the antenna function (and prevent the concentration quenching [12]). Between photosynthetic organisms, the photosystem architecture ranges from highly symmetric (such as the one in purple bacteria[9]) to apparently relatively disordered (for instance the core of photosystem 1 in plants [11]). Photosystem 2, one of the two photosynthetic light-harvesting machineries of higher plants, is depicted in Figure 1. It is interesting to note the apparent local disorder and global symmetry. Next to the spatial heterogeneity, each pigment, due to a different local protein environment, has a different transition energy [13]. As a result, the excitation absorbed, for example, by an outer LHCII antenna (Figure 1, purple), has to travel through a highly structured spatial and energetic and scape, before reaching the reaction center where it can be put to use.

Frenkel excitons

The excited electrons in photosynthesis form so-called Frenkel excitons [14–16]. The electron and hole are localized on the same molecule, but the excitation itself can be

Figure 1



Photosystem 2 $C_2S_2M_2$ supercomplex, view from the stromal side, rendered by VMD [47] using crystal structure 5XNL [10]. The depicted proteins are: major light-harvesting complexes LHCII (shades of purple), minor complexes CP29, CP24 (shades of green), CP43, CP47 (shades of yellow) and the core complexes D1, D2 (shades of orange) (other proteins in gray). The pigments are chlorophyll a (green), chlorophyll b (cyan), lutein, neoxanthin (shades of yellow) and viola/zeaxanthin (pink).

delocalized over a number of interacting pigment molecules. The properties of these Frenkel excitons (their energy, extent of delocalization, dynamics) are given by the electronic coupling between the pigments, the pigment transition energies and the interaction of the pigment electrons with the nuclear modes in their environment. While strongly coupled, near-isoenergetic pigments share delocalized excitons, a strongly interacting environment and large energy gaps localize the excitation on a few or even individual pigments. Importantly, neither of these factors is static; due to the nuclear motion they are fluctuating across many timescales, from high-frequency intramolecular vibrations to slow protein motion. As a result, the properties of the excitons are also dynamic. This paints an interesting picture of photosynthetic light harvesting. The excitation travels through a complex, ever-changing spatio-energetic landscape, in a partially localized and partially delocalized, wavelike fashion. Here we discuss the effects stemming from the interplay of energetic disorder and excitonic delocalization.

(De)localization

Let us start by considering energy transport through the photosystem in two limitting cases of a completely delocalized and a localized excitation. In the localized case, the energy landscape is directly given by the energies of the individual pigments, taking into account the polarization of their (protein) environment. The excitation is' hopping' between the pigments, performing a sort of biased random walk. As shown already by Duysens, and later

experimentally demonstrated by exciton annihilation experiments [17,18] the excitation could manage to perform a significant number of hops during its lifetime; in principle it thus has more than enough time available to reach the reaction center. However, the firm connection of the spatial and energetic basis has consequences. The energy of the localized excitonic states directly fluctuates with the pigment transition energies, possibly making the energy landscape quite unstable. Due to the energetic disorder, the excitation tends to get stuck in low-energy states. To achieve directionality in the transfer, there has to be a downhill energy gradient across the photosystem (the energy funnel concept [1]). However, with the large size of the photosystem and the corresponding high number of steps needed, this would result in too large energy losses due to thermalization. The excitation thus inevitably encounters local high-energy barriers, which are difficult to overcome for localized excitons. An advantage of a localized excitation is the possibility of the existence of variety of transfer pathways, possibly avoiding (or utilizing, if needed) trap states. In the opposite case of a completely delocalized excitation, such as in crystalline material, there is no spatial directionality, the excitation has the same probability of moving towards and away from the reaction center. The energy eigenstates, equal superpositions of excited pigment states without spatial dependence, are the preferred basis [19]. Any trap (including but not restriced to the reaction center) can very efficiently capture the excitation. This is the reason why deep defect states are a detrimental problem in semiconductor photovoltaics. In photosynthesis, however, these low-energy states can have a functional role [20•]. Compared to an ordered, crystalline material, the light harvesting membrane is a highly disordered environment. This disorder necessarily produces some degree of Anderson-type exciton localization [21]. At the same time, the high pigment concentration leads to strong interpigment interactions, producing delocalized states. The photosynthetic excitons are thus partially delocalized and partially localized. This interplay of disorder and delocalization leads to a rich and complex behaviour.

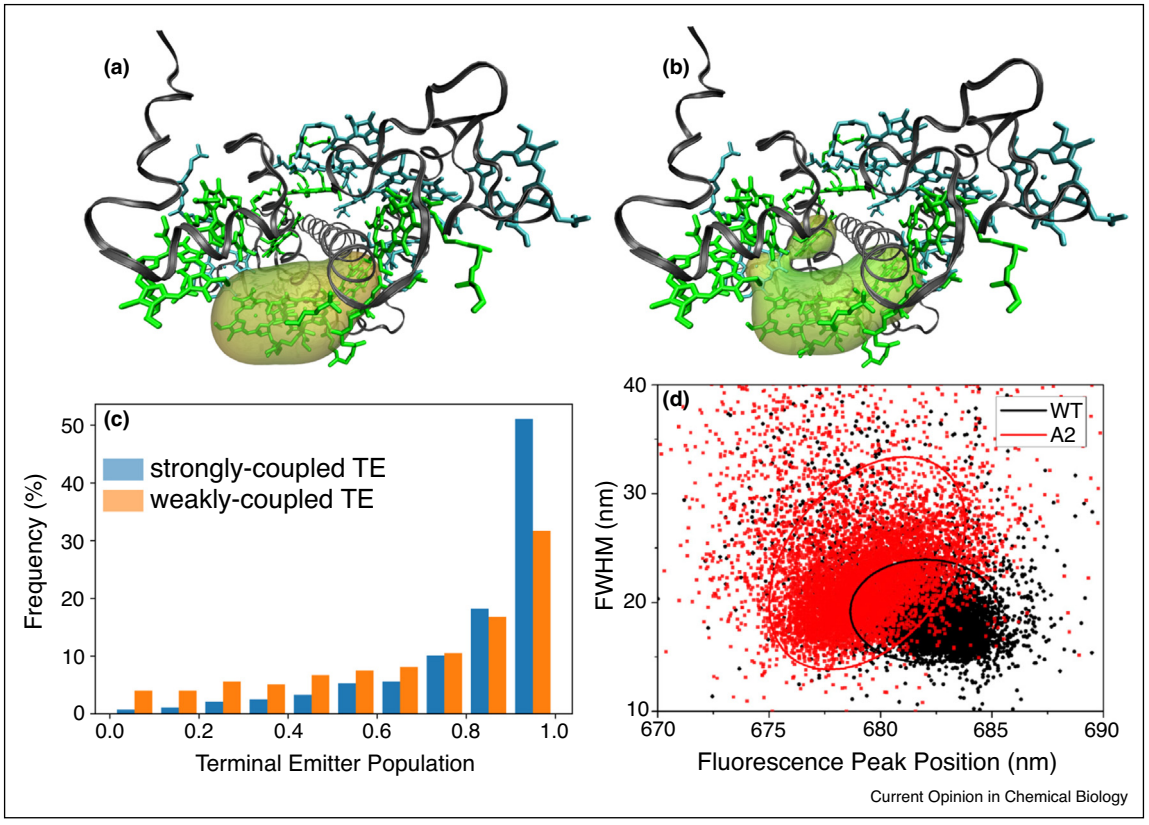
Light-harvesting complex II of higher plants

To demonstrate the perks of partial delocalization, we will focus on LHCII, the major light-harvesting complex of plants (purple in Figure 1). This antenna is composed of three chemically identical protein units, each binding 8chl a, 6chl b and 3/4 carotenoid pigments. LHCII absorbs light across most of the visible light spectrum and within a few picoseconds transfers the excitation energy to a so-called terminal emitter group of strongly coupled pigments at the periphery of the antenna [22]. This determined destination for the excitation enables the function of the antenna, either facilitating transfer to a neighboring complex or providing a place to target for energy dissipation [23]. Such a mechanism can work only when the excitation is at least partially localized. Interestingly, were the terminal emitter states fully localized on the pigments, the final state would be more sensitive to disorder compared to the case when the excitation is delocalized. In Figure 2 the excitation probability density, averaged over energetic disorder, is calculated for the natural case of a strongly coupled terminal emitter (a) and for a hypothetical case when all the couplings associated with the terminal emitter are 100 times reduced (b). In Figure 2c the distribution of probability for the excitation to end up on the terminal emitter is depicted, again for these two cases. As is apparent, the increased coupling and therefore increased delocalization leads to a final state less susceptible to disorder. A strong local delocalization over a group of pigments therefore can lead to a global localization of the excitation on a particular position in the antenna, thereby directing the energy transfer. These observations were corroborated by single-molecule spectroscopy measurements, where the emission from the terminal emitter (hence its name) is observed. A natural, wild-type LHCII was compared to a mutant where the terminal emitter was disrupted by removing two of the participating pigments. As a result, the energy and composition of the final state became significantly more disordered [24•], as evidenced by the emission, Figure 2d. Without the strong coupling, there is a significant fraction of complexes (seen in the ensemble way) where the excitation ends up at a different pigment. Interestingly, there are different organisms, diatoms, which prefer the disordered state in their light harvesting antenna FCPa/b. Apparently the disadvantage of decreased stability is outweighed by the advantage which they get by a larger fraction of states with lower energy, enabling harvesting of light towards the red part of the absorption spectrum [25]. These results demonstrate the role of delocalization and how its optimal extent can depend on the environmental conditions.

Light-harvesting complex 2 of purple bacteria

Another example of much-studied photosynthetic organisms is purple bacteria. In contrast to plants, their light-harvesting antennae called LH2 and LH1 consist of highly symmetric, circular arrangements of small transmembrane α-helical Bchl-binding proteins [26]. Due to the homogeneity of the photosynthetic membrane, there is no need for a preferred direction of energy transfer between the LH2 antennas. The directionality of transfer to the reaction-center encircling LH1 antenna is for a large part provided by the energetic funnel. Also, unlike plants, the purple bacteria have no need for switching the antenna to an energy-dissipative state as they have other ways to avoid photodamage. The emphasis in the antenna design is then put on speed and robustness of the energy transfer. It was found that the excitation is on average highly delocalized over a significant part of the ring, 4–5 BChls [27–29]. This delocalization speeds up the transfer within the rings by the wavelike excitation transfer [30]. Interestingly, the delocalization was also shown to enable

Figure 2



Delocalization within terminal emitter for robust localization on the outside of the antenna. **(a,b)** Excited state equilibrium in LHCII monomeric unit at 77 K, averaged over 110 cm^{-1} energetic disorder (Hamiltonian taken from [48]). Density is calculated excitation probability distribution, energy is colour-coded (red is low). A: strongly- and B: weakly- coupled terminal emitter pigments. **(c)** Distribution of the population of the terminal emitter pigments, in case of weak and strong interpigment coupling. **(d)** Distribution of single LHCII fluorescence peak position and width, measured by single-molecule spectroscopy. Compared is the wild type (WT) LHCII and mutant (A2) complex with perturbed terminal emitter, taken from [24•] with permission from Elsevier.

a faster transfer between the rings [31]. The reason can be seen by generalizing the Förster formula to clusters of pigments [32]. When the pigments in the clusters are strongly coupled, the energy jumps between partially delocalized excitons from the two groups, which can be faster than the mere hopping between weakly coupled pigments. Moreover, by a combination of single-molecule and ensemble ultrafast spectroscopy, we were able to observe how the protein motion causes the energetic disorder in individual LH2 complexes. We have found that the LH2 antenna is constructed in such a way that the excitation remains delocalized in the presence of the protein fluctuations [33•]. This results in a robust, energetically stable and fast energy-transferring state.

Vibronic effects

So far, we have discussed mainly the electronic states, while the 'bath' of vibrations was taken as an environment enabling energy transfer and causing exciton localization. In the last decade, though, a new role was discovered for high-frequency vibrations strongly coupled to the electronic transitions. These pronounced modes can mix with the electronic degrees of freedom, producing so-called vibronic states [34–36,37•,38]. The mixed exciton-vibrational states can then result in excitation delocalization over neighbouring pigments, even in case they are separated by a large energy gap [39,40]. The vibronic effects are currently an intensely studied topic and their detailed description is beyond the scope of this review. The presence of these vibronic states, among other effects, strengthens the role of delocalization in these energetically disordered systems.

Conclusions

Thanks to the advance of experimental methods with high spatial and temporal resolution, a wealth of information about photosynthetic light harvesting has been obtained over the last decades. Detailed structures of many of the photosystems, including their building blocks, have become available with atomistic resolution, and the excitation transfer dynamics can be followed with femtosecond precision. Although great in its potential,

such detailed information also requires attention to its interpretation, as it often brings together concepts from different scientific disciplines. When using the structural information to infer excitation transfer pathways, one should pay attention to the delocalized nature of the excitons. This often does not come natural to structural biologists [10,11]. When analyzing time resolved spectroscopy measurements obtained using femtosecond laser pulses, one should bear in mind the difference from the operation under natural 'solar' conditions [41•]. By the turn of the millennium the notion of delocalized photosynthetic excitons was firmly established in the field, based on decades of combined theoretical and experimental effort [15]. The delocalization was further confirmed by the observed presence of off-diagonal, oscillatory signals in two-dimensional electronic spectroscopy [42•,43,44]. These experiments attracted a lot of attention from other fields, such as quantum optics, quantum information and quantum computing [45]. In the world of quantum computing it seems staggering that delocalized states, quantum superpositions of excitations dwelling on several pigments, survive in the disordered natural environment. Accustomed to omnipresent decoherence, one could expect this delocalization to be something fragile [43,46]. However, the opposite is true. The excitons, like true quasi-particles, form the preferred basis and are stable against perturbations. Even more, not only are the delocalized photosynthetic excitons robust against environmental fluctuations, it is the excitonic delocalization that provides the robustness in the dynamically disordered pigment-protein complexes.

Conflict of interest statement

Nothing declared.

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